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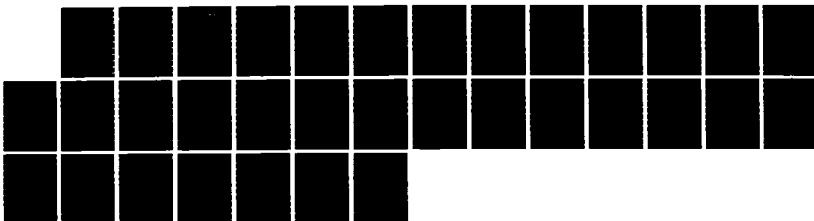
SPECTRO-ELECTROCHEMISTRY OF COBALT AND IRON  
TETRASULPHONATED PHTHALOCYANINES(U) YORK UNIV NORTH  
YORK (ONTARIO) DEPT OF CHEMISTRY M A NEVIN ET AL.  
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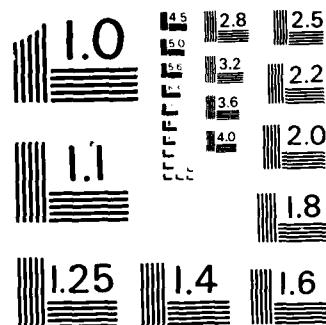
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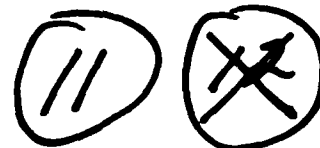
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Spectro-Electrochemistry of Cobalt and Iron Tetrasulphonated Phthalocyanines

BY

W.A. Nevin, W. Liu, M. Melnik and A.B.P. Lever

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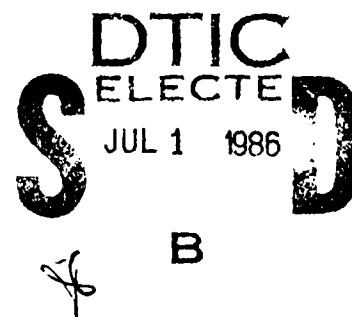
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Abstract cont'd

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## Spectro-Electrochemistry of Cobalt and Iron Tetrasulphonated Phthalocyanines

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## Abstract

Cobalt and iron derivatives of tetrasulphonated phthalocyanine (TsPc) have been studied by spectro-electrochemistry in aqueous solution at pH 2-10. For CoTsPc, two reduced species are observed: yellow  $[\text{Co(II)TsPc(-2)}]^-$  and pink  $[\text{Co(II)TsPc(-3)}]^{2-}$ , over the entire pH range. In acid, oxidation gives a monomeric  $[\text{Co(III)TsPc(-2)}]^+$  species; in base, an equilibrium exists between monomeric and dimeric forms of  $[\text{Co(III)TsPc(-2)}]^+$ , whose relative concentration depends upon concentration of CoTsPc, ionic strength, pH and temperature. Reduction of  $[\text{Fe(III)TsPc(-2)}]^+$  solutions gives green Fe(II)TsPc(-2) and pink  $[\text{Fe(II)TsPc(-2)}]^-$  over the entire pH range. Oxidation gives a product which appears to be an  $[\text{Fe(IV)TsPc}]^{2+}$  species. Differences between the spectra of the species and in the species obtained at different pH values, and aggregation effects are discussed with reference to the nature of axial coordination to the central metal atoms.

The development of suitable electrocatalysts for the reduction of oxygen at a fuel cell cathode remains an important objective. Many research groups are investigating macrocyclic  $\text{MN}_4$  systems as being likely to fulfil the many stringent requirements for a successful commercial electrocatalyst [1-10].

Recently we were involved in an electrochemical study [11] of the oxygen

reduction properties of tetrasulphonatophthalocyanine (TsPc) derivatives of cobalt and iron, CoTsPc and FeTsPc. The catalysts were deposited, at monomolecular levels, on an ordinary pyrolytic graphite (OPG) electrode. Under an inert atmosphere, a series of four redox couples were observed for FeTsPc and three for CoTsPc, corresponding to a sequence of one-electron redox processes, proven by coulometry. The redox waves exhibited varying dependence upon pH. Since the redox process may occur at either the central metal ion or the phthalocyanine ring, there is possible ambiguity concerning the actual process occurring at a given wave and such processes may vary with pH.

For example, in the case of FeTsPc, the first reduction potential showed a 59mV/decade dependence upon pH in the alkaline region, but 0mV/decade dependence in the acid region. This variation in behaviour might signify the presence of valence isomers such that, for example, reduction of Fe(II)TsPc(-2) in the alkaline range might yield  $[\text{Fe(I)TsPc(-2)}]^-$ , but in the acid range,  $[\text{Fe(II)TsPc(-3)}]^-$  might be formed. Such distinctions are difficult to draw using electrochemistry alone and spectroscopy was used to provide complementary information.

In this paper we report this spectro-electrochemistry in aqueous solution over the pH range 2-10 (at approximately constant ionic strength). The spectro-electrochemical data reveal the nature of the redox process, permit one to clarify whether a particular process might be pH dependent, and provide additional information such as degree of aggregation or the presence of dimerisation. Note further that these data represent the first detailed set of electronic spectra reported for series of redox related phthalocyanine species in aqueous phase.

The nomenclature MTsPc is used for a general species of undefined oxidation state, while, for specific compounds, the oxidation states of both metal and phthalocyanine are defined. The Pc(-2) state is the standard

oxidation state for the phthalocyanine ring [12].

### Experimental

The MTsPc (M= Co, Fe) species were prepared according to Weber and Busch [14]. Excess sodium salts were removed using dialysis tubing.  $\text{Na}_2\text{SO}_4$  (Anachemia, reagent grade) was purified by recrystallisation from aqueous solution.  $\text{NaHCO}_3$  and NaOH (BDH, analytical grade) were used as supplied. Water was purified by double distillation over  $\text{KMnO}_4$  followed by passage through a Barnstead organic removal cartridge and two Barnstead mixed resin ultrapure cartridges. Solutions were made up in the following commercial buffer solutions: (pH) 2.0, KCl, HCl, 0.05M; 4.0, potassium biphthalate, 0.05M; 7.0,  $\text{KH}_2\text{PO}_4$ , NaOH, 0.05M; 10,  $\text{K}_2\text{CO}_3$ ,  $\text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ , KOH, 0.05M (all Fisher certified and used as supplied). A second pH10 buffer was prepared using  $\text{NaHCO}_3$  (0.08M) and NaOH (0.0088M).

Electronic spectra were recorded with a Hitachi-Perkin Elmer microprocessor model 340 spectrometer or a Guided Wave Inc. model 100-20 Optical Waveguide Spectrum Analyser with a WW100 fibre optic probe. Electrochemical data were collected with a Pine model RDE3 double potentiostat or with a Princeton Applied Research (PARC) model 173 potentiostat or with a PARC model 174A Polarographic Analyzer coupled to a PARC model 175 Universal Programmer. Room temperature spectro-electrochemical measurements were made with an optically transparent electrode (OTE) assembly utilising a gold minigrid, with platinum counter and silver quasi-reference electrodes [15], which fitted into the sample compartment of the Hitachi-Perkin Elmer model 340 spectrometer. For experiments at temperatures between 0 and 80°C, a bulk electrolysis cell was used, consisting of a cylindrical platinum gauze working electrode, silver wire quasi-reference and platinum flag counter electrode (the latter separated from the working compartment by a glass frit). Spectra were



recorded during bulk electrolysis by immersing the Guided Wave fibre optic probe into the solution. Solutions were purged continuously with nitrogen gas.

Electron spin resonance data were obtained using a Varian E4 spectrometer calibrated with diphenylpicrylhydrazide. The species were generated 'in situ', in the esr cavity, using a cell based on a published design [16]. A gold coil was used as a working electrode, silver foil as a quasi-reference, and platinum flag (separated by a glass frit) as counter electrode.

Solutions for spectro-electrochemistry and esr-electrochemistry usually contained 0.3M sodium sulphate as supporting electrolyte.

## Results and Discussion

### Cobalt Tetrasulphonatophthalocyanine Derivatives

#### Co(II)TsPc(-2)

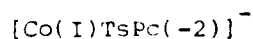
CoTsPc, in aqueous solution, has been shown to exist as an equilibrium between monomeric and dimeric (aggregated) six-coordinate Co(II)TsPc(-2) species, where the relative concentrations of monomer and dimer are extremely sensitive to a number of factors, such as concentration, pH, ionic strength and temperature [17-28]. Five-coordinate species may also be present [11]. Our experiments were carried out using aqueous solutions of CoTsPc in concentrations of the order of  $10^{-4}$ M and added electrolyte at 0.3M. Under these conditions, the phthalocyanine is expected to exist predominantly in the aggregated form, possibly through hydrogen bonding linkage (via water) of the TsPc rings [23] or through overlap between the  $\pi$ -electron clouds of the two TsPc rings [28,29]. This aggregation is

manifest in the electronic spectrum, shown in Fig.1, which consists of a broad Q band [20] of maximum 622nm, expected for the aggregate [17,19-27], and only a shoulder at 665nm, where the maximum of the monomer occurs (663nm [21-23]). Under the CoTsPc and electrolyte concentrations used here, the spectrum varied little over the pH range 2-10, in contrast to a previous pH dependence study [27], where a substantial increase in monomer content was found at higher pH values, even at  $10^{-4}$ M concentration. This is the result of the high ionic strength of our solutions (0.3M  $\text{Na}_2\text{SO}_4$ ) which promotes extensive aggregation even at high pH values, where the negative charges on the TsPc rings might tend to inhibit close association.

Hence, CoTsPc is predominantly in the  $[\text{Co(II)TsPc}(-2)]_2$  form in the starting solutions. As with other MTSPcs, there may be some higher aggregated forms present [30-32], especially as a result of the high ionic strengths used [21,22]. However, such higher aggregates are not expected to be important in the CoTsPc case [23].

CoTsPc exhibits three redox couples in the region -1.5 to +0.9V vs SCE, two couples (labelled [11] B,A; 2,1 in acid and base respectively) correspond to net reduction of the bulk solution, and will be referred to here as the first and second reduction waves, and one (D; 3) refers to net oxidation, and will be referred to as the first oxidation wave.

#### Reduction Species



Formation of the first reduction product was carried out by polarising the gold minigrid at ca. 200mV negative of the first reduction wave. At all pH values studied (pH2,4,7,10), the colour changes from blue to yellow; the spectrum is essentially independent of pH in the range studied and an example, at pH2, is shown in Fig.1 with data reported in Table I. The yellow colour arises from the appearance of a strong band in the 440-480nm region,

seen previously in chemically and electrochemically generated  $[\text{Co(I)TsPc}(-2)]^-$  species [17,33-37]. This new band has been assigned as metal to ligand charge transfer (MLCT), from  $\text{Co(I)Pc}[d(xz,yz)]$  to  $\pi^*(1b_{1u})\text{Pc}$  [35,38,39]. Notably this MLCT band is shifted by 20-30nm to higher energy in aqueous solution relative to  $[\text{Co(I)TsPc}(-2)]^-$  [17] and other  $\text{Co(I)Pc}$  species [33,35-37] in organic solutions (Table I), and also to the tetracarboxyphthalocyanine (TcPc) cobalt(I) species in water [10]. The intensity of the MLCT band is greater than the intensity of the Q band, also in contradistinction to organic phase data [17,33,35-37]. The spectrum agrees well with previous aqueous phase data obtained via  $[\text{BH}_4]^-$  reduction of  $\text{Co(II)TsPc}(-2)$ , although the relative intensities were not given [37]. ESR signals observed with  $\text{Co(II)TsPc}(-2)$  at pH2 and 10, disappeared upon reduction, consistent with the formation of diamagnetic  $d^8$   $[\text{Co(I)TsPc}(-2)]^-$  [17,36,37].

This difference in spectra between aqueous and organic phase probably reflects a difference in structure, which is also likely to be related to the chemistry of these species. Thus, the organic phase  $\text{Co(I)Pc}$  species reacts with protons to yield  $\text{Co(II)Pc}$  [33], while the aqueous species as a monolayer on ordinary pyrolytic graphite, or in solution, is stable in fairly strong acid and, evidently, does not react with protons. The reason for this variation in behaviour is being sought.



The ease of formation of the second reduced species was strongly dependent upon the pH of the solution. Previous work [11] has shown that the second reduction potential is very pH dependent. At pH2, the couple lies only 200mV negative of the first reduction wave, at a value of -0.55V vs sce; however, at pH10, the couple lies at ca. 700mV negative of the first reduction wave, at -1.25V vs sce.

Unfortunately, it was only possible to record the electronic spectrum of this species at low pH values, with the results shown in Fig.1 and Table I. Formation of the species is characterised by a change in colour from yellow to pink. There is a red-shift of the Soret, MLCT and Q bands. The MLCT band splits into two components, and there is evident structure in the Q band. This species has previously been positively identified as  $[\text{Co(II)TsPc(-3)}]^{2-}$  [36,39]. Structure in the Q band is expected for a monoanion radical [39]. There are again characteristic differences between the spectrum of this species in water, and the spectrum of the unsubstituted species in dimethylformamide (DMF) [36], with the Q band being more intense, relative to the MLCT band in aqueous solution.

At pH7 and 10, rapid evolution of gas at the working electrode at potentials negative of the second reduction wave, made it impossible to obtain the spectrum of the fully reduced species. However, the spectrum of a pink solution containing both the first and second reduced products could be 'deconvoluted' to show that the same product,  $[\text{Co(II)TsPc(-3)}]^{2-}$ , is also produced at these pHs, and, moreover, that its spectrum is hardly altered from that in acid medium. Thus, this anion radical species of Co(II) may be assumed to be formed over the entire pH range studied.

#### Oxidation Species

Oxidation of the  $\text{Co(II)TsPc(-2)}$  starting solution, by applying a potential 200mV positive of the first oxidation wave, yielded spectra which proved to be markedly pH dependent. At pH2 and 4, a blue-green colour developed; the spectrum is shown in Fig.2(a), with data in Table I. The Q band (and Soret) red shifts some 45nm relative to the starting solution and becomes narrower. This spectrum is typical of that previously defined for  $\text{Co(III)TsPc(-2)}$  species in water, prepared by chemical means [18,21,27,37]. Moreover, the increase in intensity, and narrowing, of the Q band upon

oxidation is anticipated [39]. This species is likely to be  $[(H_2O)_2Co(III)TsPc(-2)]^+$ , probably mixed with  $Cl(H_2O)Co(III)TsPc(-2)$  at pH2.

At pH7 and 10, however, oxidation results in the formation of two bands in the Q region, at 632 and 666nm, both of comparable or greater intensity to and narrower than the initial  $Co(II)TsPc(-2)$  Q band. A spectrum at pH10 is shown in Fig.2(b). However, the relative intensity of these two bands varied from sample to sample, and appeared dependent upon conditions such as concentration of  $Co(II)TsPc(-2)$  and  $Na_2SO_4$ , and pH value. In particular, decreasing the concentration of  $Co(II)TsPc(-2)$  yielded a much stronger band at 666nm relative to 632nm on oxidation such that oxidation of a  $1 \times 10^{-5}M$   $Co(II)TsPc(-2)$  solution gave a spectrum in which the 666nm band was dominant and the 632nm band barely present. The spectrum obtained upon oxidation of a solution of  $5 \times 10^{-5}M$   $Co(II)TsPc(-2)$  is shown in Fig.2(c). Decreasing the concentration of electrolyte also led to a decrease in the intensity of the band at 632nm, as shown in Fig.2(d). Once equilibrium had been reached, the relative intensities of the two bands remained constant. Increasing the potential did not significantly affect the relative intensities until potentials close to the solvent limit were reached, when the intensity of the 632nm band declined; however some decomposition also occurred.

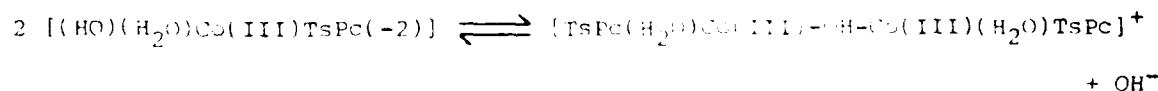
The possibility that one band arises from  $Co(II)TsPc(-2)$  generated in a chemical or electrochemical reaction between oxidation product and a solute was excluded from the insensitivity of the spectrum to potential and on the basis that switching off the potentiostat had little effect upon the spectrum.

Cooling the solution to 0°C had little effect upon the relative peak ratios, though increasing the temperature to 80°C caused a decrease in the 632nm absorption and an increase in the intensity of the 666nm band. Cooling to room temperature restored the original spectrum. Addition of DMF caused the disappearance of the 632nm band and a spectrum which appeared

very similar to that obtained in acid medium. Thus, there are two species in equilibrium and it is most reasonable to assume they both contain Co(III).

Previous work on MTSPCs has shown that raising the temperature [26,40], decreasing the ionic strength [14,21,23,25,40] or addition of DMF [41] results in disaggregation of the dimeric species. Thus, the data point strongly to a monomeric Co(III)TsPc species yielding the 666nm absorption, and a binuclear species yielding the 632nm absorption.

Co(III) complexes are almost invariably six-coordinate. The TsPcCo(III)/Co(II) couple shifts 59mV/decade with pH above pH7, but there is no shift below pH7 [11]. These data strongly suggest the existence, in basic solution, of species such as  $[(HO)_2Co(III)TsPc(-2)]^-$  and  $(HO)(H_2O)Co(III)TsPc(-2)$ . These probably contribute to the 666nm absorption. Aggregation of these species is unlikely, since the axial groups will tend to keep the TsPc units apart. However, Co(III) complexes readily form binuclear hydroxo-bridged species [42]. Thus, the 632nm absorption probably arises from such a hydroxo-bridged binuclear species in equilibrium with the six-coordinate mononuclear species cited immediately above, i.e.



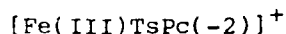
666nm

632nm

Binuclear oxo-bridged  $PcM-O-MPc$  species ( $M=Al(III)$ ,  $Cr(III)$ ,  $Mn(III)$ ,  $Fe(III)$ ) are well known [43-47], and yield blue-shifted  $\pi$  bands generally absorbing near 620nm. There is also the possibility that the 632nm absorption arises from such a  $TsPcCo(III)-O-Co(III)TsPc$  species; however, no such  $\mu$ -oxo-bridged porphyrin or phthalocyanine complexes of Co(III) have been previously unequivocally characterised.

In acid solution,  $\text{Co(III)TsPc}(-2)$  probably exists in the form  $[(\text{H}_2\text{O})_2\text{Co(III)TsPc}(-2)]^+$  [11]. The presence of two strongly bound axially coordinated water molecules should prevent dimerisation, resulting in the occurrence of only a monomeric species in solution, absorbing at 668nm, with a vibrational component at 605nm. However, unlike  $\text{Co(III)Pc}$  species in organic solvents [33,35,37,48], the  $\text{Co(III)TsPc}$  spectrum in acid solution is broader and contains a shoulder at 635nm, indicating the presence of a small amount of aggregated species. Possibly this may occur via hydrogen bonding between the two axial water molecules. No previous study of the dimerisation of  $\text{Co(III)TsPc}$  has been reported. It is relevant to note that whereas the amount of aggregation increases with decreasing pH for the  $\text{Co(II)TsPc}(-2)$  species [27], an opposite effect is found with pH for the  $\text{Co(III)TsPc}(-2)$  species. Thus at pH7, the band at 666nm is stronger, relative to the 632nm band, compared with a pH10 solution. However, there is an abrupt transition to the monomeric species spectrum below pH7, such that at pH5.5, a similar spectrum to pH2 is obtained. This reversal in behaviour between  $\text{Co(II)}$  and  $\text{Co(III)}$  is due to the formation of the hydroxo-bridged species at high pH.

#### Iron Tetrasulphonatophthalocyanine Derivatives



In the presence of air, solid  $\text{FeTsPc}$  exists as an  $\text{Fe(III)}$  species in the form of an oxygen adduct [14]. In aqueous solution, prepared in air, an  $\text{Fe(III)TsPc}(-2)$  species is obtained, possibly also in the form of an oxygen adduct [18], or as  $[(\text{H}_2\text{O})_2\text{Fe(III)TsPc}(-2)]^+$  in aqueous acid, or  $(\text{HO})(\text{H}_2\text{O})\text{Fe(III)TsPc}(-2)$  in aqueous alkali [11]. In parallel with  $\text{CoTsPc}$ , a monomer-dimer equilibrium exists, dependent upon pH, concentration, ionic strength and temperature [25,40]; however, the tendency to form dimers and poly-aggregated species appears greater for  $\text{FeTsPc}$  than for  $\text{CoTsPc}$  [40]. The

spectrum of a typical Fe(III)TsPc species, prepared for electrolysis at pH10, is shown in Fig.3 with tabulation in Table II. As expected the dimeric, aggregated form predominates, as shown by the broad Q band centered at 632nm [14,18,25,40,49-51]. The weak shoulder at 670nm probably arises from a small amount of monomeric material [40]. At the high FeTsPc and electrolyte concentrations used here, higher polyaggregates are probably present [40]. The spectrum was essentially unaltered over the pH range studied (2,4,7,10), in agreement with published results [25,40], and was identical before and after degassing. At least in alkaline solution, contributions from  $\mu$ -oxo species are anticipated; these however, would also absorb near 630nm and may be difficult to detect spectroscopically [43,45,51].

FeTsPc exhibits four redox couples in the region -1.4 to +0.9V vs SCE, corresponding to three successive reductions of the bulk material (labelled [11] C,B,A; 3,2,1 in acid and base respectively) and one oxidation of the bulk material (D; 4).

#### Reduction Species

##### Fe(II)TsPc(-2)

Formation of Fe(II)TsPc(-2) directly from the Fe(III) species by electrolysis some 200mV negative of the Fe(III)/Fe(II) couple (C; 3) (referred to as the first reduction couple) was progressively more difficult with increasing pH. Thus, at pH10, prolonged electrolysis produced only a broad band at ca. 666nm (due to Fe(II)) with a prominent shoulder at 630nm believed to be due to un-reduced Fe(III)TsPc(-2).

The Fe(II) product was, however, readily generated by polarising the electrode negative of the second reduction wave (Fe(II)/Fe(I)), producing Fe(I)TsPc (see below), and re-oxidising by polarisation at a potential



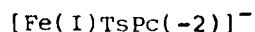
positive of the Fe(II)/Fe(I) couple but negative of the Fe(III)/Fe(II) couple. This produced a spectrum (Fig.3, Table II) whose Q band intensity was about one-third larger than that of the band produced, in alkaline medium, by one-electron reduction of Fe(III)TsPc. At pH 2 and 4, this Fe(II)TsPc(-2) spectrum could be obtained directly by one-electron reduction of the Fe(III)TsPc(-2) species.

These data can be explained if it is assumed that the relative contribution of  $\mu$ -oxo Fe(III) species, such as TsPc(-2)(H<sub>2</sub>O)Fe-O-Fe(H<sub>2</sub>O)TsPc(-2), increases with increasing pH; this is certainly not unreasonable, cf e.g. TsPcMn-O-MnTsPc species [52]. The electrochemical behaviour of a pure TsPcFe-O-FeTsPc species has not yet been characterised, however data for the unsubstituted species in pyridine has recently been reported [53]. These show a one electron reduction to a mixed valence Fe(III)-Fe(II) species occurring some 200mV negative of the Fe(III)/Fe(II) wave of the PcFe(II)Py<sub>2</sub> mononuclear complex, and complete reduction to a Fe(II)-Fe(II) species occurring 1250mV negative of the mononuclear Fe(III)/Fe(II) couple. Similarly, reduction of the analogous PcMn-O-MnPc species [44], and of  $\mu$ -oxo[bis(tetraphenylporphyrin)Fe(III)] [54] occurs significantly to more negative potentials than the corresponding wave in the mononuclear analogues. Thus, the Fe(III)/Fe(II) reduction couple in TsPcFe(III)-O-Fe(III)TsPc will be shifted negative of that of the monomeric (and aggregated dimeric) species. The residual 630nm absorption in the spectrum of reduced species at potentials only 200mV negative of the Fe(III)/Fe(II) couple (due to non-oxo species) must then originate in un-reduced  $\mu$ -oxo species remaining in solution. Reduction negative of the second reduction potential (to Fe(I)), reduces the total Fe(III)TsPc component and removes the  $\mu$ -oxo species thereby. In acid solution, the  $\mu$ -oxo species cannot exist and the problem does not arise. A similar problem arose with the reduction of Fe(III)TcPc(-2) [10] in alkaline

solution. There was residual absorption near 630nm due to the unreacted Fe(III)TcPc  $\mu$ -oxo species, present in the Fe(II)TcPc(-2) spectrum, but its presence was not recognised.

The green Fe(II)TsPc(-2) species was unequivocally defined by its electronic spectrum [18,50], especially by the observation of a band near 440nm commonly seen in low-spin six-coordinate Fe(II) phthalocyanine species [10,35,55-59] and associated with the Fe(II)-axial ligand interaction [10,57-59]. The spectrum was independent of pH.

The spectrum does show indications of aggregation in both acid and alkaline medium. The broadening of the Q band absorption near 630nm in acid solution cannot arise from a  $\mu$ -oxo Fe(III)TsPc contaminant since this would not exist in this medium. A rigorously six-coordinate species is not likely to show aggregation because of steric constraints. Either the coordinated water molecules are labile, allowing one to be replaced by another Fe(II)TsPc(-2) moiety, or there is a small contribution from five-coordinate species, which could aggregate.



Reduction at ca. 200mV negative of the second reduction couple, yields a pink solution, whose principal feature is an intense new band at ca. 490nm and a red-shifted and weakened Q band, compared with Fe(II)TsPc(-2) (Fig.3, Table II). The spectrum is similar to that previously reported for  $[\text{Fe(I)TsPc(-2)}]^-$ , obtained by  $[\text{BH}_4]^-$  reduction of the Fe(III)TsPc species in  $\text{H}_2\text{O}/20\% \text{ DMF}$  [49], and that obtained through electrochemical generation from Fe(II)Pc [36,55]. The intense band near 490nm is undoubtedly MLCT in origin, in parallel with  $[\text{Co(I)TsPc(-2)}]^-$  described above. Aggregation does not seem to be important in either the acidic or basic range, perhaps because the negative charge tends to keep the molecules apart. However, unlike the cobalt(I) species, the spectrum of the iron(I) species is dependent upon pH,

with red shifts of both the MLCT and Q bands with increasing pH, though the overall spectroscopic pattern does not change (Table II).  $[\text{Fe}(\text{I})\text{Pc}(-2)]^-$  is known to coordinate axial ligands to form five-coordinate species [55]. The potential of the  $\text{Fe}(\text{II})/\text{Fe}(\text{I})$  couple shows no dependence per pH decade, in the basic region [11]. It is unlikely that there would be axial hydroxide bound to  $\text{Fe}(\text{I})$ , so there can be no axial hydroxide bound to  $\text{Fe}(\text{II})$ . However we do anticipate water coordination to  $\text{Fe}(\text{II})\text{TSPc}(-2)$ . Possibly the difference between acidic and basic medium could be ascribed to axial coordination of water in acidic medium, and no axial ligand in basic medium.

The same situation arises in the  $[\text{Co}(\text{I})\text{TSPc}(-2)]^-$  case discussed above. The absence of a dependence of the  $\text{Co}(\text{I})$  spectrum on pH may mean that water is coordinated to  $[\text{Co}(\text{I})\text{TSPc}(-2)]^-$  in both the acidic and basic regimes, or that the extra electron in this species, along the axis, weakens the axial interaction to such an extent that it has little perturbing effect on the electronic spectrum.

The MLCT band is blue-shifted by 25-30nm for the  $[\text{Fe}(\text{I})\text{TSPc}(-2)]^-$  species in pH10 solution, compared with  $[\text{Fe}(\text{I})\text{Pc}(-2)]^-$  [36,55] and  $[\text{Fe}(\text{I})\text{TSPc}(-2)]^-$  in  $\text{H}_2\text{O}/20\% \text{DMF}$  [49], while the Q band is red-shifted by 40-50nm and is of lower intensity relative to the MLCT band. This species was easily obtained at pH10; however, it became progressively more difficult to obtain at lower pH values due to decomposition of the phthalocyanine and evolution of gas at the electrodes at the required potentials. For the most part, decomposition involved destruction of the phthalocyanine ring and loss of visible region absorption. In particular, at pH2, it was not possible to obtain a pure species, though the appearance of a pink color and spectrum, similar to that at pH10, indicates that an  $[\text{Fe}(\text{I})\text{TSPc}(-2)]^-$  species is still obtained.

The overall conclusion is that  $[\text{Fe}(\text{I})\text{TSPc}(-2)]^-$  is formed over the entire pH range studied, at potentials some 200mV negative of the second

reduction couple.



Although the third reduction couple occurs only ca. 200mV negative of the second at pH2 and 4 [11], we were unable to obtain a satisfactory spectrum of this species due to gas evolution and decomposition of the phthalocyanine. An impure species spectrum was obtained at pH10 (Table II). This showed a lower intensity MLCT band at 490nm, and additional bands at 370, 650 and 730nm. The similarity of this spectrum to that reported for  $[\text{Fe(II)Pc(-3)}]^{2-}$  [36], and for  $[\text{Fe(II)TsPc(-3)}]^{2-}$ , produced by  $[\text{BH}_4]^-$  reduction of  $\text{Fe(III)TsPc}$  in  $\text{H}_2\text{O}/20\%$  pyridine [49], and to the spectrum reported here for  $[\text{Co(II)TsPc(-3)}]^{2-}$  leaves little doubt that, at pH10, this anion radical species of  $\text{Fe(II)TsPc}$  is the third reduction product. By analogy with  $\text{CoTsPc}$ ,  $[\text{Fe(II)TsPc(-3)}]^{2-}$  is also expected to be the third reduction product (couple A) in acid solution.

#### Oxidation Species

Oxidation of an  $[\text{Fe(III)TsPc(-2)}]^+$  species in the OTE assembly, at a potential positive of the first oxidation couple resulted in the growth of a new band at 680nm, at the expense of the  $\text{Fe(III)TsPc}$  Q band absorption. The Soret peak was broadened into a shoulder. However, the phthalocyanine decomposed rapidly, so that there was a general loss in overall intensity of the chromophoric species. Decomposition could be reduced, but not stopped, by carrying out the oxidation at  $0^\circ\text{C}$ , when the spectrum shown in Fig.4 was obtained (see also Table II). The oxidation is reversible, in that the original  $\text{Fe(III)TsPc(-2)}$  spectrum can be obtained by electrolysis 200mV negative of the first oxidation wave, but the overall intensity thereof, is reduced. The spectrum shown in Fig.4 is quite different from those of  $\text{X}_2\text{Fe(III)Pc(-1)}$  and  $\text{X}_2\text{Co(III)Pc(-1)}$  films [13] ( $\text{X} = \text{a halogen}$ ) and from  $\text{X}_2\text{Co(III)Pc(-1)}$  in chloroform

[48], where these phthalocyanine ring-oxidised radical species were produced by halogen oxidation of the M(II)Pc precursors. The spectrum does not contain the extra features expected for a phthalocyanine oxidised ring species [39], but rather, looks more like the spectrum of a MPc(-2) species. Thus, these data provide evidence for formulation as an Fe(IV)TsPc(-2) species, at pH7. Further experiments are in hand to seek a solvent where this species might be stable for more detailed study.

### Summary

The redox couples A-D or 1-4 (in acid or base, respectively [11]) for CoTsPc and FeTsPc have been defined by spectro-electrochemistry over the pH range 2-10. For FeTsPc, couples A, B and C correspond to  $[\text{Fe(II)TsPc(-2)}]/[\text{Fe(I)TsPc(-2)}]^-$  and  $[\text{Fe(III)TsPc(-2)}]^+ / [\text{Fe(II)TsPc(-2)}]$ , respectively. Couple D has been shown to be probably  $[\text{Fe(IV)TsPc(-2)}]^{2+} / [\text{Fe(III)TsPc(-2)}]^+$ , rather than the expected ligand oxidation.

For CoTsPc, couples A and B (1 and 2), in a similar manner to FeTsPc, are  $[\text{Co(II)TsPc(-2)}]/[\text{Co(I)TsPc(-2)}]^-$  and  $[\text{Co(III)TsPc(-2)}]^+ / [\text{Co(II)TsPc(-2)}]$ , respectively. Some uncertainty was present in the voltammograms in acid solution in the earlier study [11] in the oxidation region, where an ill-defined wave (labelled C) was seen, followed by a wave D at higher potential. We have shown that couple D (and 3 in base) is in fact due to the  $[\text{Co(III)TsPc(-2)}]^+ / [\text{Co(II)TsPc(-2)}]$  couple, and hence the broad region C may be due to the existence of variously aggregated Co(II)TsPc(-2) species.

Several trends in the pH dependence of formation of the redox species are likely due to differences in axial coordination of the central metal atoms. In addition, it is interesting to note some differences in dimer formation between the iron and cobalt species (Table III). Aggregation of Co(II)TsPc(-2) is a result of its very labile axial water molecules. However, the  $d^6$  Fe(II)TsPc(-2)

species is not expected to be labile, and this is shown by only partial aggregation in solution. Co(III) is also  $d^6$ , and  $[\text{Co(III)TsPc(-2)}]^+$  is found to be non-aggregated (in acid solution) as a result of the non-lability of its axially coordinated water molecules. In contrast, Fe(III)TsPc(-2) is fully aggregated in acid solution due to the lability of its axial ligands (ca  $10^{-4}\text{M}$ , high ionic strength).

In base, the tendencies of Co(III) and Fe(III) to form hydroxy- and  $\mu$ -oxo-bridged species, respectively, are manifested in the spectro-electrochemistry of  $[\text{Co(III)TsPc(-2)}]^+$  and  $[\text{Fe(III)TsPc(-2)}]^+$  at pH 7-10, which is markedly different from that found in acid solution.

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unit in its standard oxidation state. The first ring oxidised species is the radical  $Pc(-1)$  and the first ring reduced species is the radical  $Pc(-3)$  [13]. The charge due to the presence of deprotonated sulfonic acid residues is ignored in the formulae presented in this paper.

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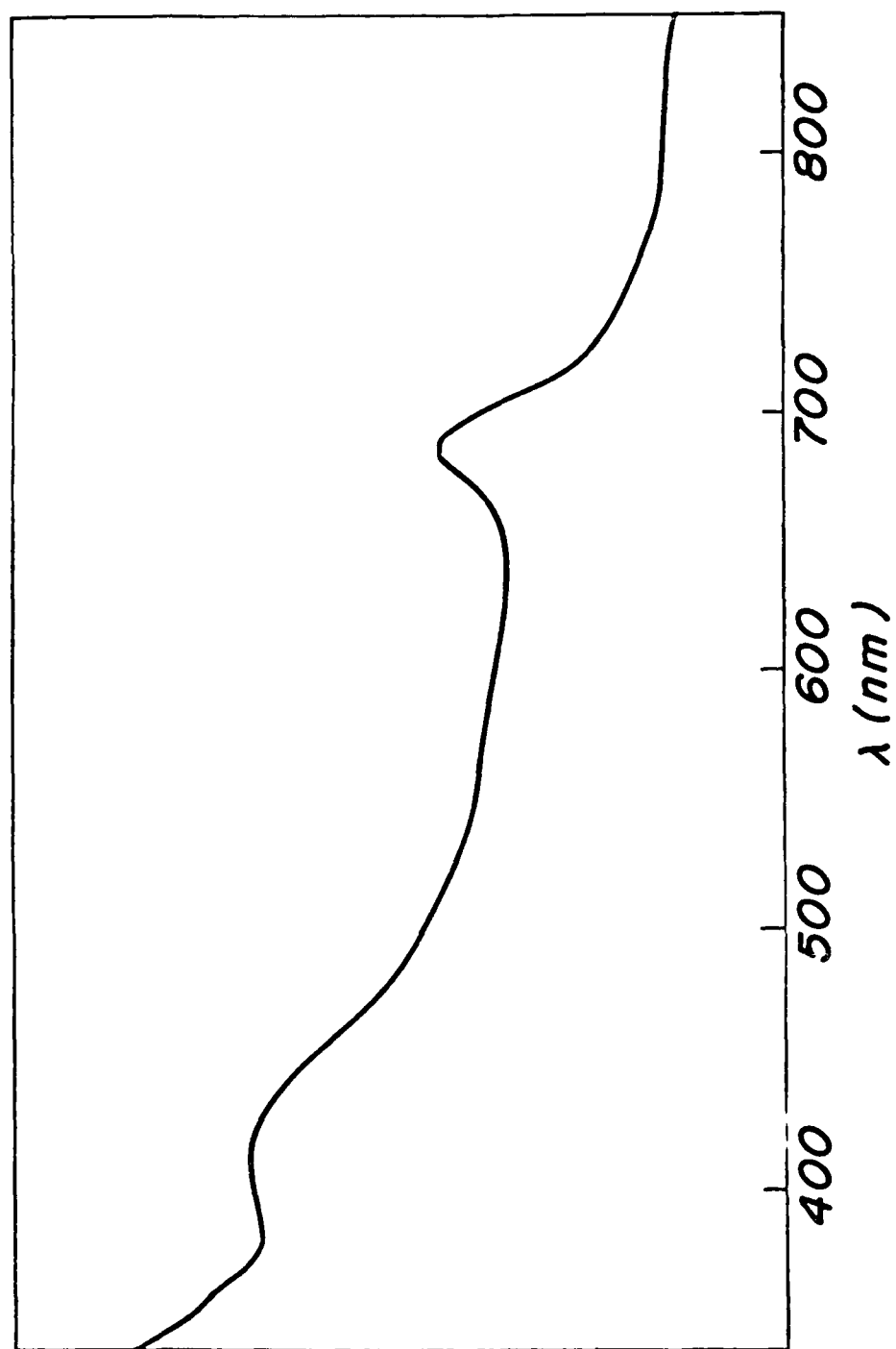
## Figure Legends

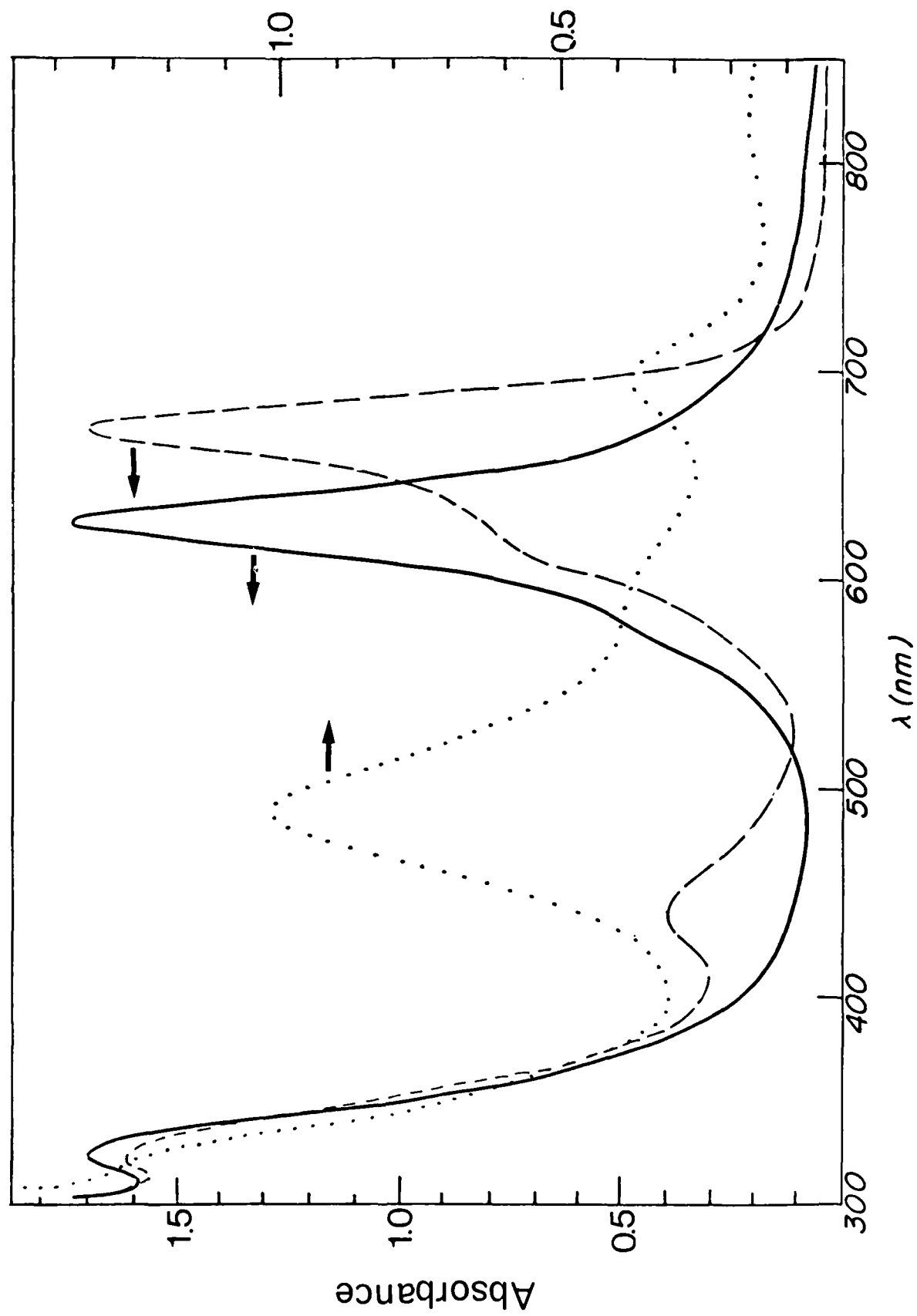
Fig.1. Uv-visible absorption spectra of (a)  $\text{Co(II)TsPc(-2)}$  (\_\_\_\_), and electrochemically generated  $[\text{Co(I)TsPc(-2)}]^-$  (----) and (b) electrochemically generated  $[\text{Co(I)TsPc(-3)}]^{2-}$ .  $[\text{CoTsPc}] = 5 \times 10^{-4}\text{M}$ ,  $[\text{Na}_2\text{SO}_4] = 0.3\text{M}$ , pH 2. Spectra taken with OTE.

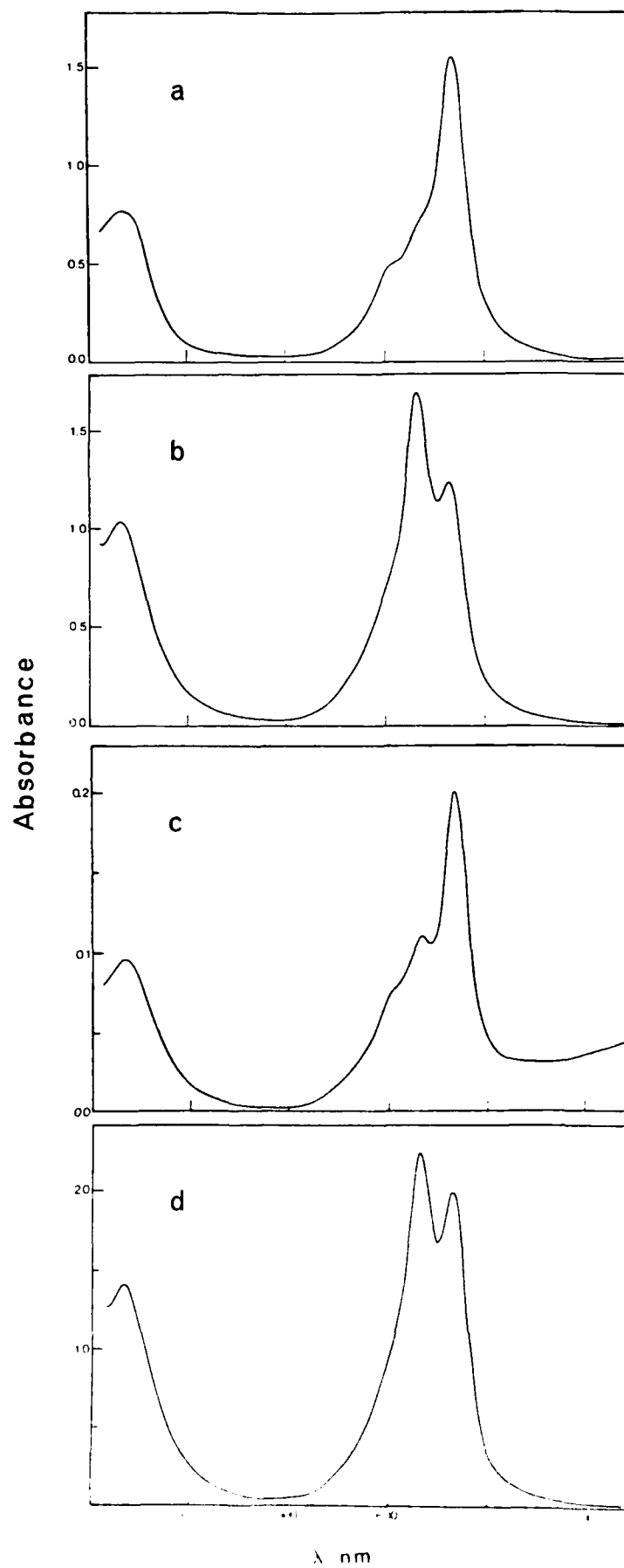
Fig.2. Uv-visible absorption spectra of electrochemically generated  $[\text{Co(III)TsPc(-2)}]^+$ : (a) pH4,  $[\text{CoTsPc}] = 5 \times 10^{-4}\text{M}$ ,  $[\text{Na}_2\text{SO}_4] = 0.3\text{M}$ ; (b) pH10,  $[\text{CoTsPc}] = 6 \times 10^{-4}\text{M}$ ,  $[\text{Na}_2\text{SO}_4] = 0.3\text{M}$ ; (c) pH 10,  $[\text{CoTsPc}] = 5 \times 10^{-5}\text{M}$ ,  $[\text{Na}_2\text{SO}_4] = 0.3\text{M}$ ; (d) pH10,  $[\text{CoTsPc}] = 7 \times 10^{-4}\text{M}$ ,  $[\text{Na}_2\text{SO}_4] = 0.08\text{M}$ . Spectra taken with OTE.

Fig.3. Uv-visible absorption spectra of  $[\text{Fe(III)TsPc(-2)}]^+$  (\_\_\_\_), and electrochemically generated  $\text{Fe(II)TsPc(-2)}$  (-----) and  $[\text{Fe(I)TsPc(-2)}]^-$  (.....) species.  $[\text{FeTsPc}] = 6 \times 10^{-4}\text{M}$ ,  $[\text{Na}_2\text{SO}_4] = 0.3\text{M}$ , pH 10. Spectra taken with OTE.

Fig.4 Uv-visible absorption spectrum of electrochemically oxidised  $[\text{Fe(III)TsPc(-2)}]^+$ . Initial concentration of  $\text{FeTsPc} = 2 \times 10^{-5}\text{M}$ ,  $[\text{Na}_2\text{SO}_4] = 0.3\text{M}$ , pH 7, Temp. =  $25^\circ\text{C}$ . Spectra taken with a fibre optic probe.







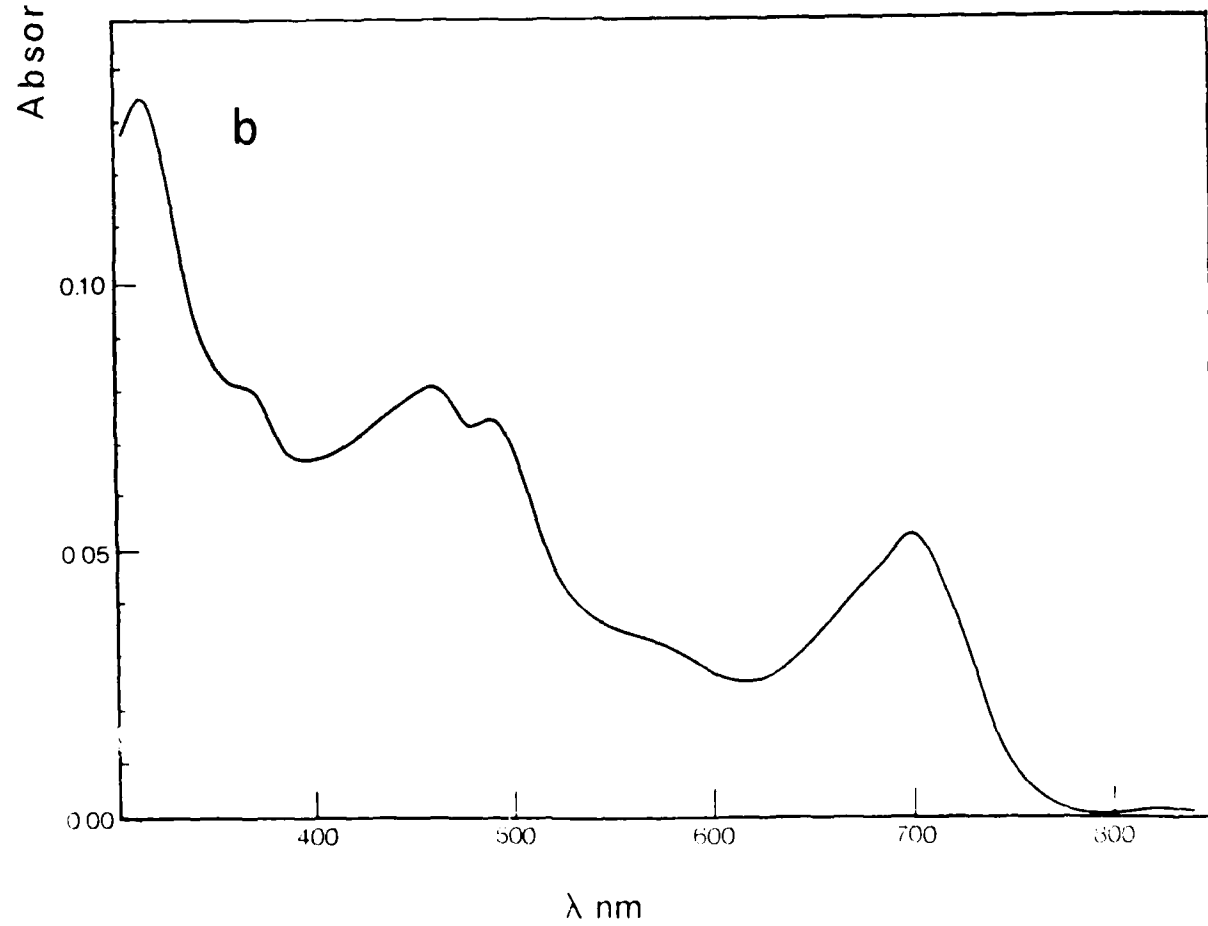
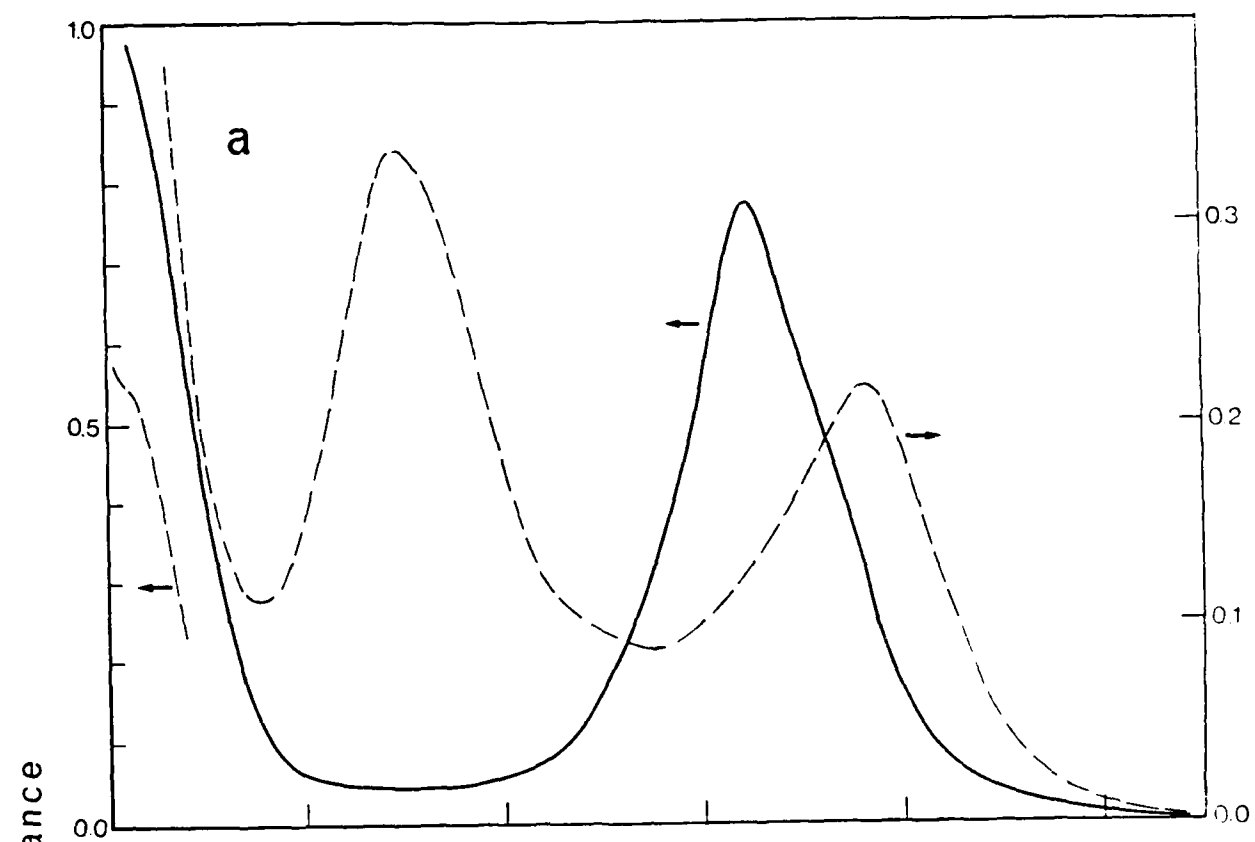


TABLE III. Summary of CoTsPc and FeTsPc Redox Species Obtained in Acidic ( $\text{H}_3\text{O}^+$ ) and Basic ( $\text{OH}^-$ ) Aqueous Solution and Extent of Aggregation.<sup>a</sup>

CoTsPc			FeTsPc		
Couple <sup>b</sup>	$\text{H}_3\text{O}^+$	$\text{OH}^-$	Couple <sup>b</sup>	$\text{H}_3\text{O}^+$	$\text{OH}^-$
D, 3	$[\text{Co(III)TsPc(-2)}]^+$ , non-aggregated	$[\text{Co(III)TsPc(-2)}]^+$ , non-aggregated	C, 3	$[\text{Fe(III)TsPc(-2)}]^+$ , aggregated	$[\text{Fe(III)TsPc(-2)}]^+$ , aggregated
		$[\text{TsPc(-2)Co(III)-OH-Co(III)TsPc(-2)}]^+$			$[\text{TsPc(-2)Fe(III)-O-Fe(III)TsPc(-2)}]$
B, 2	$\text{Co(II)TsPc(-2)}$ , aggregated	$\text{Co(II)TsPc(-2)}$ , aggregated	B, 2	$\text{Fe(II)TsPc(-2)}$ , partly aggregated	$\text{Fe(II)TsPc(-2)}$ , partly aggregated
	$[\text{Co(I)TsPc(-2)}]^-$ , non-aggregated	$[\text{Co(I)TsPc(-2)}]^-$ , non-aggregated		$[\text{Fe(I)TsPc(-2)}]^-$ , non-aggregated	$[\text{Fe(I)TsPc(-2)}]^-$ , non-aggregated
A, 1	$[\text{Co(II)TsPc(-3)}]^{2-}$ , non-aggregated	$[\text{Co(I)TsPc(-3)}]^{2-}$ , non-aggregated	A, 1	$[\text{Fe(II)TsPc(-3)}]^{2-}$ , non-aggregated	$[\text{Fe(II)TsPc(-3)}]^{2-}$ , non-aggregated

a. Axial ligands are omitted.

b. A-D and 1-3 refer to the redox couples obtained in acidic and basic solution, respectively, as given in ref.11.



TABLE II. Electronic Absorption Maxima (nm) of Fe/TSPc Species.<sup>a,b</sup>

pH	Fe(III)TSPc(-2)	Fe(II)TSPc(-2)	Fe(I)TSPc(-2) <sup>c</sup>	Fe(IV)TSPc(-2)
2.0	326 (1.03) 580 632 670 (sh) (1.0) (sh)	326 440 610 635 667 (0.98) (0.18) (sh) (sh) (0.83)	470 610 670 (0.10) (sh) (0.07)	
4.0	326 580 632 665 (0.98) (sh) (1.0) (sh)	326 435 635 666 (sh) (0.23) (sh) (0.94)	330 470 610 670 (sh) (0.14) (sh) (0.10)	
7.0	326 580 632 670 (1.01) (sh) (1.0) (sh)	325 435 610 635 668 (0.98) (0.18) (sh) (sh) (0.80)	320 494 610 696 (sh) (0.33) (sh) (0.10)	350 419 682 810 (sh) (0.10) (0.06) (vw)
10.0	326 580 630 670 (1.0) (sh) (1.0) (sh)	322 440 620 669 (0.93) (0.22) (sh) (sh) (0.99)	320 488 600 698 820 (sh) (0.54) (sh) (0.15) (0.03)	
Py		330 414 593 654 (7.6) (1.9) (3.0) (10.7) <sup>d</sup>	327 515 595 661 801 (2.5) (2.5) (1.1) (1.5) (1.2) <sup>e</sup>	

sh = shoulder, vw = very weak  
 $[\text{Fe(III)TSPc}(-2)] = 1-6 \times 10^{-4} \text{ M}$ ;  $[\text{Na}_2\text{SO}_4] = 0.3 \text{ M}$

- The numbers in brackets give the absorbances of the peaks relative to the 0 band (510) of the initial Fe(II)TSPc solution. The reduction of Fe(II)TSPc to Fe(I)TSPc(-2) was monitored by the appearance of a new absorption band at 470 nm. Note that some decomposition of phthalocyanine has occurred for the reduced and oxidized species, resulting in the formation of a new absorption band at 820 nm in the 3-6.5 M region.
- An impure spectrum was also obtained for the species Fe(II)TSPc(-3) in pH 6 solution, absorbing at 470 nm. The spectrum of Fe(II)TSPc(-3) in pH 6 solution is shown in Figure 1.
- The spectra at pH 2 and 4 contain some Fe(II)TSPc(-2) impurity.
- Ref. 39; e. ref. 45; data for Fe(IV)(Py)<sub>2</sub>; values in brackets are  $\epsilon \times 10^3$ ; Py = pyridine.

TABLE I. Electronic Absorption Maxima (nm) of CoTsPc Species.<sup>a</sup>

pH	Co(II)TsPc(-2)	Co(III)TsPc(-2)	Co(1)TsPc(-2)	Co(1)TsPc(-3) <sup>b</sup>
2.0	320 570 622 665 (sh) (sh) (1.0) (sh)	333 345 605 635 667 (0.71) (sh) (sh) (sh) (1.06)	310 448 540 610 680 (sh) (0.43) (sh) (sh) (0.28)	310 365 460 490 570 700 810 (0.17) (sh) (0.10) (0.09) (sh) (0.07) (w)
4.0	320 570 622 665 (sh) (sh) (1.0) (sh)	334 345 605 635 668 (0.62) (sh) (sh) (sh) (1.24)	310 448 540 610 680 (sh) (0.42) (sh) (sh) (0.30)	
7.0	320 570 622 665 (sh) (sh) (1.0) (sh)	332 345 600 632 666 (0.75) (sh) (sh) (0.96) (1.01)	310 448 540 610 682 (sh) (0.55) (sh) (sh) (0.38)	322 370 462 570 690 820 (0.10) (w) (0.10) (sh) (0.08) (w)
10.0	320 570 622 665 (sh) (sh) (1.0) (sh)	332 600 632 665 (0.78) (sh) (1.28) (0.93)		
DMSO <sup>c</sup>	332 600 663 (6.9) (3.2) (12.9)		330 465 645 710 (5.0) (4.5) (1.8) (8.3)	

sh = shoulder, w = very weak, br = broad  
 $[\text{Co(II)TsPc(-2)}] = 5 - 6 \times 10^{-4} \text{ M}$ ;  $[\text{Na}_2\text{SO}_4] = 0.3 \text{ M}$ .

- a. The numbers in brackets give the absorbances of the peaks relative to the Q band (=1.0) of the initial Co(II)TsPc(-2) solution before electrolysis. Note that for the reduced species, some decomposition of phthalocyanine has occurred, resulting in disruption of the Pc ring and loss of absorption in the w-visible region. Decomposition products did not absorb in the 300-850 nm region.
- b. The spectrum at pH 10 is a mixture of Co(1)TsPc(-2) and Co(1)TsPc(-3) (ca. 20:80 ratio).
- c. Ref. 17; values in brackets are  $\epsilon \times 10^{-4}$ ; DMSO = dimethylsulphoxide.

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